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GRAPHIC STUDIES OF ULTIMATE ANALYSES OF COALS

BY

OLIVER C. RALSTON

WITH A PREFACE BY

HORACE C. PORTER



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PREFACE.

By HORACE C. PORTER.

As an aid to the study of the constitution and origin of coal a systematic survey of a large number of chemical analyses of various coals is of undoubted value, but as a basis for classifying the different kinds of coal, its value may be questioned.

When it is considered that the organic substance of certain bituminous coals has almost exactly the same ultimate composition as has cresol— $C_6H_4(OH)CH_3$ —or benzyl alcohol— $C_6H_5CH_2OH$ —a hint is given of the difficulty of classifying organic materials by their ultimate analyses. Owing to the immense possibilities of polymerism and isomerism in carbohydrate and, especially, cellulosic compounds and in their degradation products, such as coal, we find differences frequently in character and behavior among materials of this nature having the same ultimate composition. Furthermore, coal is not a definite unit substance chemically, but is made up of a great variety of complex derivatives, various mixtures of which may show the same ultimate composition.

On the other hand, the classification of related organic materials that have resulted from metamorphosis in progressive stages of an original basic material may possibly be made dependent on chemical composition, as the materials distinguish themselves from each other by progressive changes in composition, always similar in character. But such a metamorphosis is complicated in many cases by the incidental introduction of another material foreign to the original base, and by the changes that it undergoes.

Graphic studies of the ultimate composition of coals, using triangular coordinates, as proposed by Grout,^a and amplified by Mr. Ralston in this paper, lead empirically to an application of the theory of progressive metamorphosis to coal. The well-defined unidirectional line of average coal composition from cellulose and starches through peat, lignite, and bituminous coals to anthracite indicates strongly a progressive uniform change from an original basic material. The anomalous position of the group of cannels is an illustration of the effect of the intrusion of a foreign material and its changes of composition into the principal series of changes.

The value of a systematic arrangement of coals by chemical composition lies in its use for classification on scientific grounds and for

^a Grout, F. F., *The composition of coals: Econ. Geol.*, vol. 2, 1907, pp. 225-241.

a study of formation and origin. Classification and nomenclature of coals on this scientific basis are desirable, although a reasonable question may arise as to the relative desirability of this basis and that of the behavior of coals in practical use. The two kinds of classification do not always agree in the grouping of coals. By ultimate analysis, for example, a certain coal may be classed as a high-grade steam or gas coal, although practically excluded from such classification by its friability, clinkering tendencies, or excessive sulphur content. The so-called "splint" coals, "smithing" coals, and "long-flaming" coals do not segregate themselves in a chemical classification. Both classification schemes, however, are of value, each for its own purpose, and it is hardly to be expected that either one alone can meet all requirements throughout the entire range of coals.

Various attempts have been made to devise formulas for classifying coals in a practical way according to proximate or ultimate analysis. Frazer's^a "fuel ratio," fixed carbon divided by volatile matter, has the virtue of simplicity, but fails to differentiate sufficiently the lower grades.

Parr^b has suggested grouping coals according to the composition of their volatile matter—the amount of inert or noncombustible matter therein, and the ratio of the total carbon in the coal to that volatilized. His scheme, although taking into account more thoroughly than others the practical behavior of coals, is inconveniently complex, and is based on wrong assumptions, namely, that all of the oxygen of coal is volatilized in union with hydrogen as water, and that all of the volatilized carbon is in a combustible form, these assumptions being far from the truth as regards lignites and subbituminous coals.

Campbell^c has proposed a classification based on the ratio of total carbon to total hydrogen, a scheme open to the objection that the hydrogen in water and the hydrogen uniting with the oxygen of the coal have a meaning entirely different from that of the "available" or fuel hydrogen. Campbell defends his use of the total hydrogen on the ground that, even combined as water, hydrogen may have a fuel value, because "in many cases," by dissociation of the water, it "becomes available for fuel purposes." It is hardly necessary to call attention to the fundamental laws which preclude the use of water as a fuel in this manner.

^a Frazer, Persifor, Classification of coals: *Trans. Am. Inst. Min. Eng.*, vol. 6, 1877-78, p. 430.

^b Parr, S. W., The classification of coals: *Jour. Am. Chem. Soc.*, vol. 28, 1906, p. 1425; The available hydrogen of coal: *Jour. Am. Chem. Soc.*, vol. 29, 1907, p. 582.

^c Campbell, M. R., Classification of coals: *U. S. Geol. Survey, Prof. Paper* 48, pt. 1, 1906, pp. 168-173.

On the basis of ultimate analyses alone, with particular reference to the oxygen content and ratios derived from it, White^a has studied and classified a large number of coals. He has not attempted to make a far-reaching classification or to group into "distinct and natural categories," which he believes to be impossible with current analytical data.^b "Classification of coals," he says,^c "on the basis of chemical analysis, must therefore be absolutely arbitrary with very finely drawn as well as purely empirical distinctions." White's system of comparing and studying coal composition involved the use of only a part of the elements of the coal. He used the ratio of carbon to oxygen plus ash, for example, on the dry-coal basis, neglecting the hydrogen; or, on the ash-free and moisture-free basis, he used the hydrogen-oxygen ratio, neglecting the carbon. Importance was placed chiefly on the oxygen in determining the character of the coal. No attempt was made to group coals by a graphic method on the basis of composition alone, as was done by Grout, and is carried out in more detail in the present paper.

Campbell,^d two years after his proposal, cited in a previous reference, suggested another and highly practical system of classification, involving chiefly the physical differences such as those of cleavage, fracture, and physical appearance in distinguishing the lower-grade coals and a grouping suggested by Grout for the higher-grade coals.

Grout's method^e was to group according to total carbon and the ratio of total to fixed carbon on the ash-free and moisture-free basis. This ratio is practically the same as Parr's ratio of total carbon to volatilized carbon, except for the omission of the factor of inert volatile matter used by Parr. In the higher-grade coals the use of these two factors, total carbon, and the ratio of total to fixed carbon, serves well to classify according to fuel value and kind, as volatilized carbon from such coals is chiefly fuel carbon. In the lower-grade coals, however, as before mentioned, volatilized carbon is rather largely in the incombustible form of carbon dioxide, and the ratio assumes a different meaning.

The triangular graphic arrangement of coals according to their ultimate analyses, first proposed by Grout and further developed by Ralston, is not primarily a classification, but rather a natural arrangement, as the coals necessarily place themselves according to composition, each element in a given coal's carbonaceous substance (free of sulphur and nitrogen) assuming its proportionate influence.

^a White, David, The effect of oxygen in coal: Bull. 29, Bureau of Mines, 1911, 80 pp. Reprint of U. S. Geol. Survey Bull. 382.

^b White, David, op. cit., p. 61.

^c White, David, loc. cit.

^d Campbell, M. R., A practical classification for low-grade coals: Econ. Geol., vol. 3, 1908, p. 134.

^e Grout, F. F., The composition of coals: Econ. Geol., vol. 2, 1907, p. 240.

Natural groupings according to properties and behavior show themselves without the aid of artificial rearrangement by ratios or functions.

The relative positions assumed naturally by different coals in the diagram, on the basis of composition, each constituent of the true coal substance being taken into account, serve to throw light upon the character of the chemical change occurring in coal formation, its degree of uniformity throughout the various stages, and the connection of the various coals and related materials with each other. The scheme is more than a classification of coals; it is a method of correlating graphically the facts afforded by coal analyses, so as to facilitate the study of their meaning in their relations to each other.

It is to be borne in mind that the errors of analysis influence the position of many coals unequally. Many of the seeming anomalies in the positions of certain coals are due to this cause, and the width of the "line" of average coal composition would undoubtedly be lessened if all inaccuracies of analysis were eliminated. The variables plotted in the diagram are percentages of carbon, hydrogen, and oxygen in the carbonaceous substance of the coal, free of all other elements—moisture, ash, sulphur, and nitrogen. Errors in the determination of all the other constituents therefore influence the oxygen figure, because it is obtained by difference, and errors in the determinations of moisture, ash, sulphur, and nitrogen influence the carbon and hydrogen figures as calculated. In a coal with a high content of sulphur, as iron pyrite, the sum of the sulphur and ash as determined is considerably higher than the actual mineral matter and sulphur present, on account of the burning of iron sulphide to oxide. This error tends to make the oxygen as determined by difference too low. In some coals the error is practically balanced by the loss of water of hydration from shale and clay in the mineral matter, but when the proportion of pyrite is high and the proportion of shale is low the error becomes important, and oxygen may easily be 0.5 per cent low on this account. Errors in other determinations may in some instances accrue in such manner as to cause a resultant oxygen error of more than 1 per cent. The error in carbon may be 0.3 per cent, in moisture 0.2 per cent, and in hydrogen and nitrogen an aggregate of 0.1 per cent.

GRAPHIC STUDIES OF ULTIMATE ANALYSES OF COALS.

By OLIVER C. RALSTON.

INTRODUCTION.

This paper presents the results of a study of the most reliable published analyses of coal. The analyses are studied from several different angles, a special type of trilinear coordinates based on that proposed by Grout^a for this purpose being used for plotting the ultimate analyses of coals in terms of the recalculated percentages of carbon, hydrogen, and oxygen, and the nitrogen and sulphur being ignored, as they are known to be, to some extent, organic constituents of the coal substance, but in very small amounts and varying according to no known laws. The analyses are calculated to a moisture-free, ash-free, nitrogen-free, and sulphur-free basis, so that $C+H+O=100$ per cent.

By the use of such a system of trilinear coordinates it is possible to represent these three variables by one point on a diagram, and a fourth variable can be plotted on an axis perpendicular to the plane of the diagram. As a fourth variable there have been used such entities as time, pressure, volatile matter, and calorific value, and the results have revealed certain facts and laws that have not been suspected, as well as showing graphically much information that has been expressed in extensive tables of figures and in long statements that have been difficult of interpretation.

It has been found that the samples of coal represented in Bulletin 22^b of the Bureau of Mines (where the first 10,000 analyses made by the United States Geological Survey and this bureau are reported), and variously described, according to the classification developed by former workers,^c as anthracite, semianthracite, semibituminous, bituminous, and subbituminous coal and lignite and peat, when plotted according to their ultimate analyses fall on the ternary diagram into certain definite fields that overlap to only a small extent. From the diagram it is evident why former workers have not been able to get

^a Grout, E. F., The composition of coals: *Econ. Geol.*, vol. 2, 1907, pp. 225-241.

^b Lord, N. Y., Analyses of coals in the United States with descriptions of mine and field samples collected between July 1, 1904, and June 30, 1910, with chapters by J. A. Holmes, F. M. Stanton, A. C. Fieldner, and Samuel Sanford: *Bull. 22, Bureau of Mines*, 1913, 1200 pp. In two parts.

^c Campbell, M. R., Hypothesis to account for the transformation of vegetable matter into the different grades of coal: *Econ. Geol.*, vol. 1, 1905, pp. 26-33; comment by Lane, A. C., p. 498.

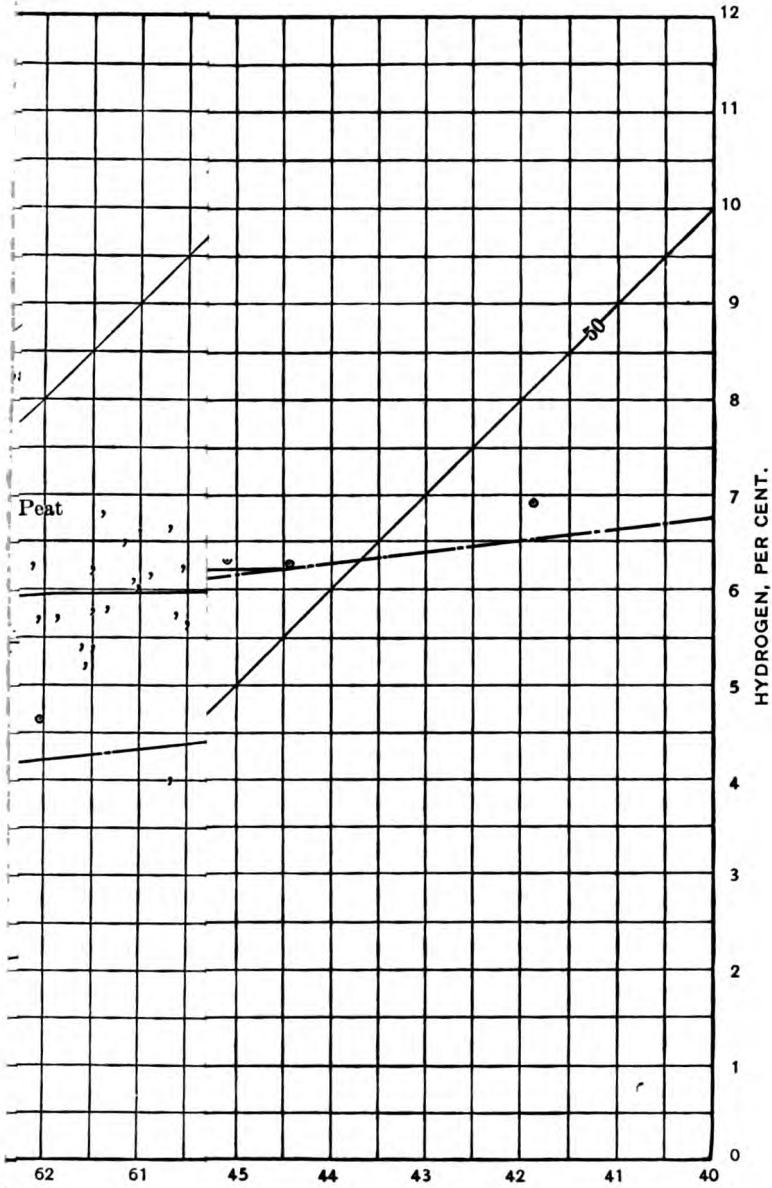
a definite line of division between the different kinds of coals, most of them having been able to plot with only two variables at one time, and none of them having been able to plot all three of the fundamental constituents—carbon, hydrogen, and oxygen. The lines of division between the fields that separate different kinds of coals on the ternary diagram would have to bear some simple relation to the axes of coordinates if any of the two-variable or three-variable methods of plotting heretofore used were to be successful, but they do not. The statement that these boundary lines would have to bear some simple relation to the axes of coordinates means that they would have to be either parallel or perpendicular to them. The mathematics of this statement will become evident after the use of the diagram has been explained.

All the coal analyses plotted fall in a rather narrow band across the diagram (Pl. I), with only one distinct curve in it. The width of this band is considerably more than that due to the total error of analysis, so that it can not be assumed that the band would narrow to a line if all of the errors were eliminated. This gives one more reason why former investigators have failed to reach conclusions that apply to all coals from the consideration of such ratios as that of carbon to oxygen or of hydrogen to oxygen, as the coals on the upper side and those of the lower side of the band differ distinctly, but otherwise are close together in composition. The ability to plot all three of these variables against one another has allowed much more rigid and valuable conclusions to be drawn. Also, the amount of available hydrogen can be read directly from the diagram, and this entity can hence be used to advantage when so desired.

Such a diagram is an aid in instructing students in the differences between fuels, as it is simple, easy to reproduce from memory, and conveys a definite picture. Moreover, the advantage, which always applies to graphic representation of data, of being able to plot thousands of coal analyses on one diagram so that their relations can be seen at a glance is evident by one look at the thin band of dots that represents all the coals that have been analyzed by the Government bureaus up to June 30, 1910.

The investigation has shown that there is a fairly definite relation between the calorific value of a coal and its ultimate analysis. If lines be drawn through dots representing coals of equal calorific value on the diagram, these "isocalorific" lines will run in a certain manner diagonally across the thin band of coals and be nearly parallel to each other and almost straight. This is an entirely empirical result and compares well with theory.

"Isovolatile" curves show a similar relation between the volatile matter of a coal and the ultimate analysis. The "isovolatile" lines



also cut diagonally across the band of dots, but in a direction opposite to that of the "isocalorific" lines.

A relationship between the moisture, as determined by the ordinary accepted methods of analysis and the ultimate analysis, is difficult to prove because of possible large variations in these methods. Only a general relation is indicated, which may be capable of verification if the conditions outlined in this paper be carried out in making moisture analyses.

Ash and sulphur being largely fortuitous components of coal, their only feature of interest as regards this research is the effect of their presence on the other constituents. Most of these effects have been mentioned many times in the literature on coal, except perhaps one, which, so far as the writer knows, was first observed during this investigation. It seems that in the great majority of cases a high sulphur content means that the coal will be high in hydrogen and volatile matter as compared with coal of ordinary sulphur content from the same bed.

As mentioned above, nitrogen constitutes only a small proportion of the coal, never varying much from 1.25 per cent, and when it does vary it is by no known law. The nitrogen content is therefore neglected and the concordance of the results seems to justify the procedure.

The author has endeavored to indicate a possible rational or mathematical method of handling data on the distillation of coals and of predicting the analysis of the gases to be obtained. Up to date little has been accomplished beyond a tabulation of results of distillations of different fuels, with small chance of coordinating the data or working out a method whereby the results might be predicted before the analysis is made. The possibilities of research along this line are great.

SCIENTIFIC AND PRACTICAL VALUE OF AUTHOR'S DIAGRAMS.

The diagrams (Pls. I, II, and III) present a tabulation of data that have never before been collected into anything like an organic whole, and it affords a wider view of the whole field of fuels than has previously been given. The fact that fairly good relations are shown between the ultimate analysis and such factors as volatile-matter content and calorific value, and possibly moisture content, can be utilized in predicting the other properties of a coal when only a few are known, as a complete analysis will not be necessary to identify a particular fuel. The author believes that the practical man will find the diagrams useful in this respect, as well as furnishing desired information which can be readily gained. The gas manufacturer will doubtless be able to modify them to his own needs and find them a

great convenience. The scientist will find here one of the nearest approaches to a mathematical treatment of all the possible alterations of fuels, and it is hoped that the different lines of research that these diagrams show possible will be aided by their use.

COORDINATES USED.

As the type of coordinates used is somewhat different from that in general use and has been developed for a particular purpose, an explanation of the ordinary trilinear coordinates, which make use of the equilateral triangle as a base, is given here, the essential features that apply to the new system of coordinates being outlined.

The fundamental theorem in geometry upon which the equilateral system of trilinear coordinates is based can be stated as follows: "In any equilateral triangle (fig. 1) the sum of the three perpendiculars

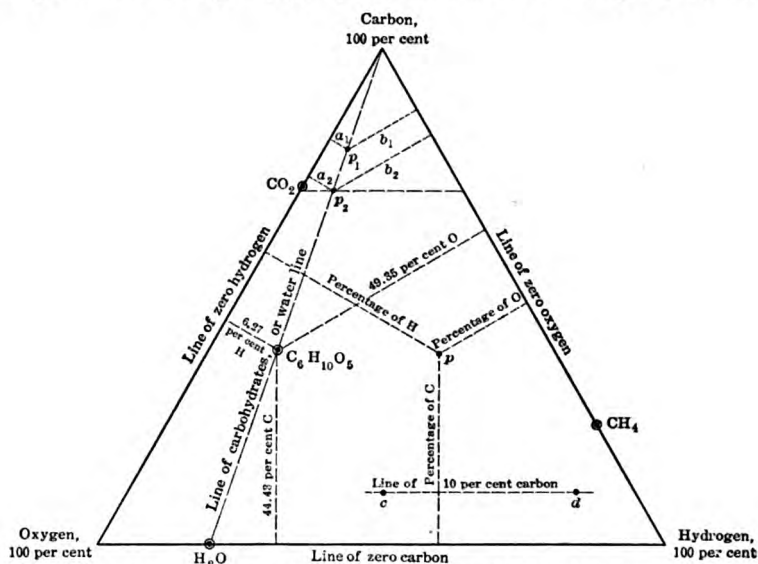
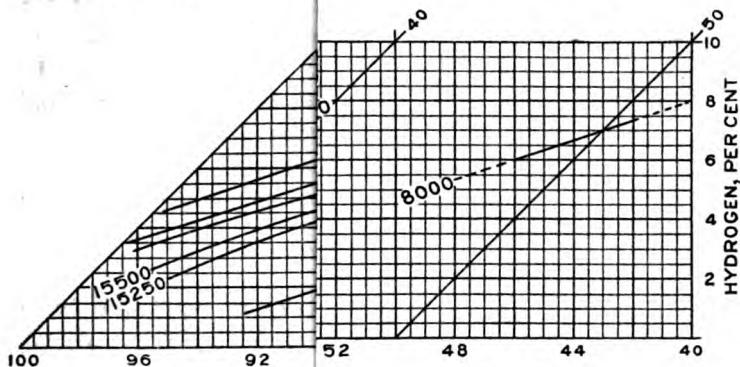
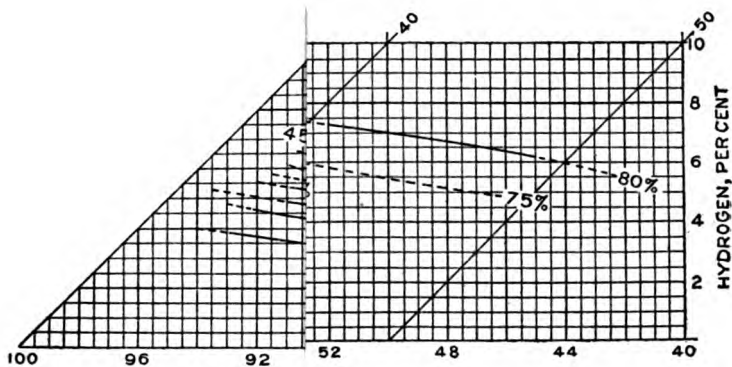


FIGURE 1.—Triangle to illustrate equilateral theorem.

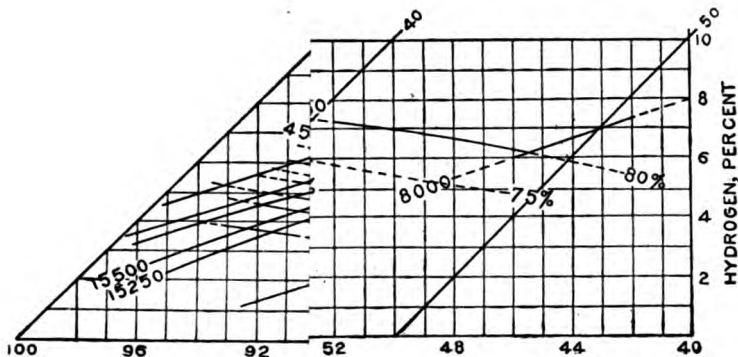
from any point, p , to the three sides of the triangle is a constant." This constant can be made 100 per cent, and each perpendicular can be made to represent the percentage of some one constituent of a ternary mixture. Thus, in the case of oxygen, hydrogen, and carbon the percentage of each in a coal can be represented by the perpendicular distance of the point representing the coal from the respective bases of the triangle. It is easily seen that any specific ternary mixture of this kind is represented by one point only within the triangle. The composition of cellulose, $C_6H_{10}O_5$, calculated to percentages by weight of each constituent, is plotted in figure 1. The analysis of a ternary mixture must be calculated to percentages by weight, which should total 100 per cent.



1
A. CURVES SHOWING γ IS DRAWN THROUGH POINTS



B. CURVES SHOWING γ CURVE IS DRAWN THROUGH



For convenience in plotting, the triangle is often ruled off into spaces for every 10 per cent or for every 1 per cent, or subdivisions of 1 per cent, if the scale used is large enough (fig. 2). An examination of figure 2 will show how a point is plotted, and anyone unfamiliar with this kind of coordinates would do well to pick out the points on this diagram representing 10 per cent and multiples of 10 per cent, such as the point representing a compound containing 70 per cent carbon, 10 per cent hydrogen, and 20 per cent oxygen.

PROPERTIES OF COORDINATES.

Several important properties of the coordinates, which apply as well to the modified form of coordinates used by the writer in classifying coals, are as follows:

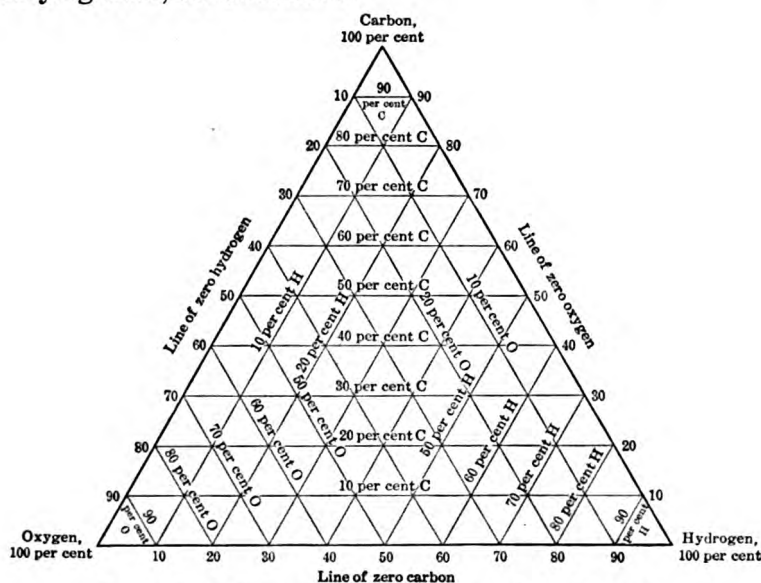


FIGURE 2.—Trilinear coordinates on an equilateral triangle.

First, a point on one of the side lines, say the one designated "H₂O" (fig. 1), is on the zero line of the element that reaches 100 per cent at the vertex opposite, and hence represents a compound that contains only two elements. Consequently, compounds containing only two elements, such as CO₂, CO, CH₄, and H₂O, will all be on one of the edges of the triangle. In the same way pure oxygen is represented by one of the vertices of the triangle where the zero lines of the other two elements meet.

Next, if a line be drawn from one vertex to an opposite side, such as the one from the carbon vertex to the point H₂O (fig. 1), then a certain simple relation exists between the coordinates of any series of points along this line. For example, consider the points p_1 and p_2 , for

which the ordinates representing the percentages of hydrogen and oxygen are a_1 , a_2 , b_1 , and b_2 , respectively. It is evident that by the application of the theorems of similar triangles the following ratio holds: $a_1 \div a_2 = b_1 \div b_2$, and the same ratio of hydrogen to oxygen holds for the points representing cellulose and water. That is to say, for all the points along this particular line the ratio of oxygen to hydrogen is constant, which, in the line chosen, happens to be the right ratio for them to form water. In other words, all of the so-called "carbohydrates" fall on this line. The same constancy of ratio holds for one of the pairs of components whenever a straight line is drawn through a vertex of the triangle.

Also for a series of points along a line parallel to one of the sides of the triangle there is a constant percentage of the constituent whose zero line is represented by that side. Such is the line cd in figure 1, where points c and d and all other points along this line would represent a constant percentage of carbon—10 per cent in this case.

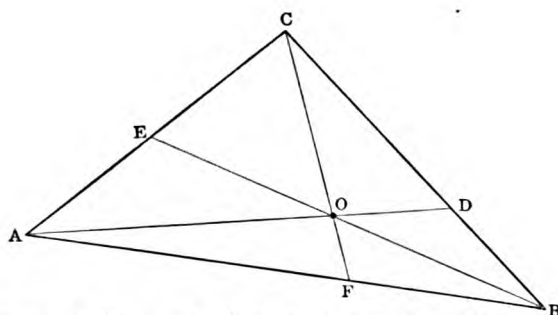


FIGURE 3.—Diagram to illustrate theorem of modified system.

Lastly, if a compound, such as cellulose (fig. 1), loses some such constituent as H_2O , the composition of the residue will have to change along a straight line drawn through the two points representing H_2O and cellulose to some point like p_1 or p_2 on the side away from the point representing H_2O . Or, if cellulose were to gain water the composition of the complex would be changed along this same straight line toward the point H_2O .

All of these properties of the equilateral trilinear diagram apply to the modified form that was used in the investigation herein reported.

MODIFICATION OF SYSTEM.

Owing to the difficulty of obtaining paper that has been ruled especially for trilinear coordinates, as well as in an effort to obtain a diagram that has certain other advantages later enumerated, a more general case of the geometric theorem on which plotting with three coordinates is based, was worked out. The theorem is stated as fol-

COAL ANALYSES.

the percentages of hydrogen and oxygen. It is evident that by the use of similar triangles the following ratio of hydrogen to oxygen holds for the line chosen, happens to be the same. In other words, all of the points on this line. The same constancy of ratio of components whenever a straight line is drawn parallel to one of the sides of the triangle.

Let a line parallel to one of the sides of the triangle be drawn, cutting the other two sides. The ratio of the segments of the sides cut by this line is constant. Such is the line *ed* in the diagram. All other points along this line have the same ratio of carbon—10 per cent in

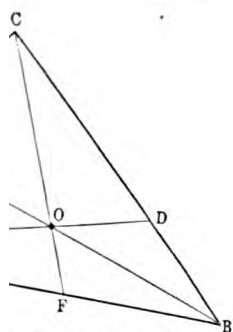


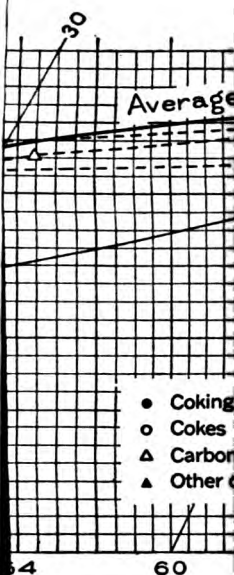
Diagram illustrating the theorem of modified system.

cellulose (fig. 1), loses some such amount of the residue will have to change. Although the two points representing the composition p_1 or p_2 on the side away from the cellulose were to gain water the composition would be changed along this same line.

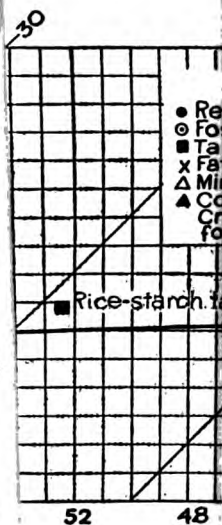
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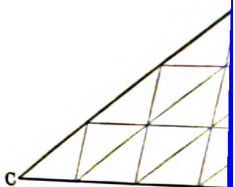
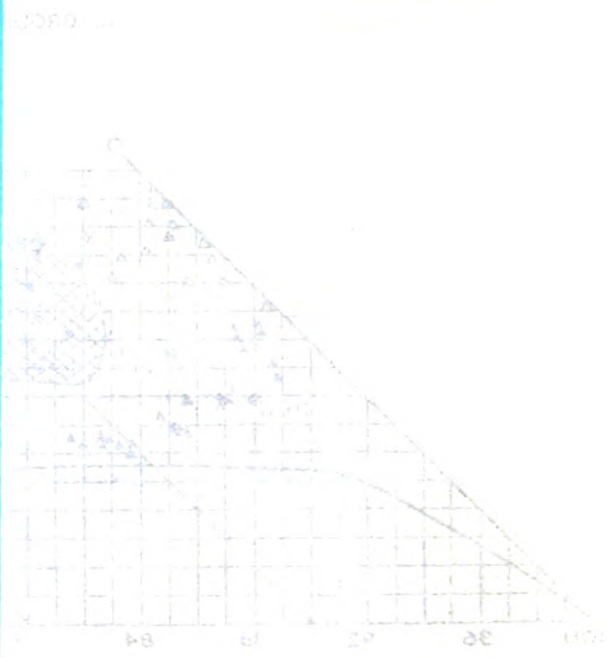
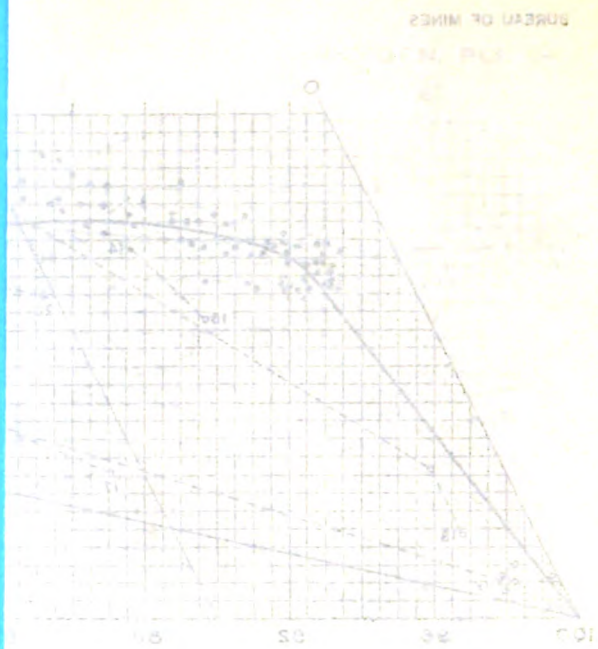


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lows: "If, in any triangle, ABC (fig. 3) lines be drawn from the vertices through any point, O, and produced to the opposite sides of the triangle, the following relation is true:

$$\frac{OD}{AD} + \frac{OE}{BE} + \frac{OF}{CF} = 1.$$

The fundamental theorem of the equilateral trilinear coordinates, previously stated, is a special case of this theorem. It is an easy step to prove that from any point, the sum of the ratios obtained by dividing the perpendiculars to the three sides by the three respective altitudes of the triangle is equal to 1. Therefore the vertical distance between each base and the opposite vertex may be divided into

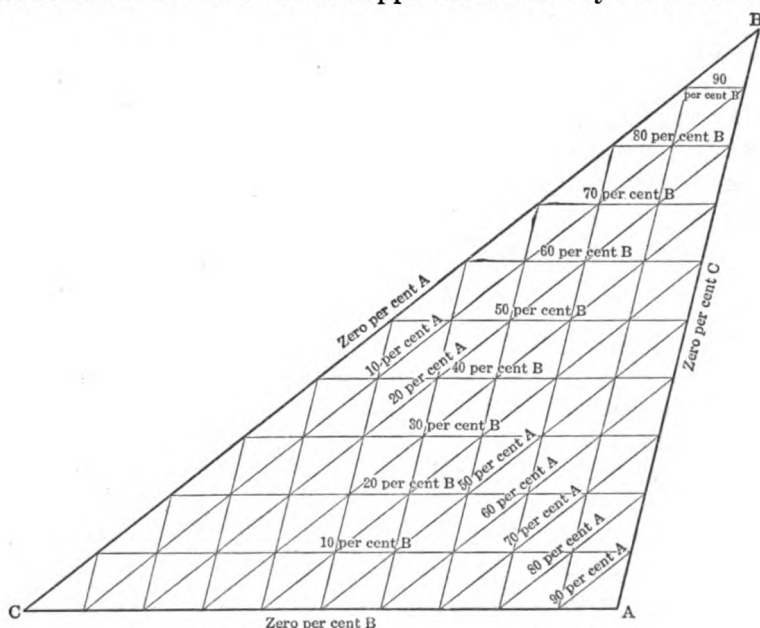


FIGURE 4.—Trilinear coordinates on an oblique triangle.

100 spaces, each representing 1 per cent, giving a diagram (fig. 4) that looks as the equilateral diagram would in a distorting mirror.

The particular form of triangle chosen as best suited for this work was the isosceles right triangle, as shown in figure 5. Two sets of the lines are at right angles to each other, and hence ordinary right-angled coordinate paper can be used for these two, so that only the oblique lines for the third set of ordinates need be added. Further consideration of the nature of these coordinates shows that it is not even necessary to draw in this third set of lines. The reason is as follows: The sum of the carbon, hydrogen, and oxygen being 100 per cent, a compound is defined by stating how much carbon and hydrogen are present, as the oxygen is necessarily the difference between the sum of these two and 100 per cent. Moreover the point can be placed on

4173°—15—3

the diagram by the use of merely two of the ordinates, though it necessarily must represent the third ordinate by its distance from the base of the third set of ordinates, consequently the ruling for the third set may be omitted. This has been done in most of the work, and for the third set of coordinates only lines representing 10 or multiples of 10 per cent were drawn. If it is important to know the values of this third set of ordinates, for any purpose whatsoever, all the lines can be ruled in, but if it is not important to know them the labor of preparing the plotting paper is small.

The third set of coordinates is relatively shorter than the other two, and as the percentage of oxygen in a coal is calculated by difference after the other constituents have been determined, the oxygen result necessarily has a higher probable error, and plotting it on the relatively shorter coordinates will in part compensate for its greater probable error. On that account this "short" ordinate was chosen for plotting the oxygen content of the coals. The application of this principle agrees well with the more or less abstruse mathematics of the theory of errors, and its further application in trilinear plotting of other systems should be of value.

Reviewing, it is evident that such a type of coordinates allows the use of ordinary cross-section paper and allows the weighting of the various probable errors of the entities plotted.

Only a part of the triangle, represented by the shaded part of figure 5, was used in most of the work, as the analyses of all of the coals, peats, etc., fall within that area. It seems remarkable

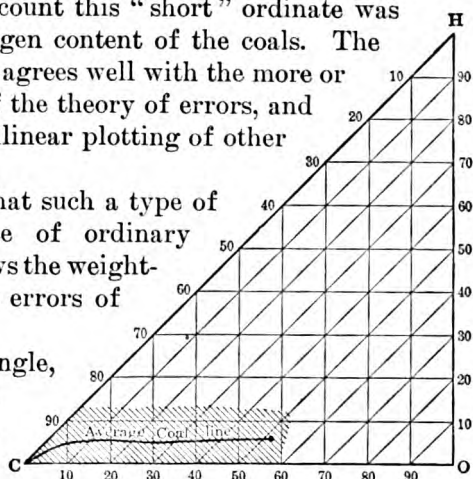


FIGURE 5. Trilinear coordinates on isosceles right triangle. Only the shaded part was used in plotting coal analyses.

that of all the organic compounds that can be represented on this diagram, all the coals should fall in such a small area and in such a narrow band across that area.

CLASSIFICATION OF COALS FROM THEIR ULTIMATE ANALYSES.

By using the special type of coordinates developed it is easy to plot all of the available coal analyses and also the analyses of peats, woods, cellulose, and other products that are supposed to be the original substances from which the coals have been derived. This has been done with all of the analyses given in Bulletin 22^a of the

^a Lord, N. W., Analyses of coals in the United States, with descriptions of mine and field samples collected between July 1, 1904, and July 30, 1910, with chapters by J. A. Holmes, F. M. Stanton, A. C. Fieldner, and Samuel Sanford: Bull. 22, Bureau of Mines, 1913, 1200 pp. In two parts.

Bureau of Mines, as well as with many other analyses by reliable analysts,^a the analyses being recalculated so that $C+H+O=100$ per cent, on a moisture-free, ash-free, nitrogen and sulphur-free basis (Pl. I).

All of these analyses lie in a thin, narrow band extending across the lower part of the diagram. At first sight it would seem that if all errors could be eliminated the band might reduce to a line, and that consequently the differences between coals were only a matter of alteration from the original substances, but on further consideration of the analyses and the probable error of the different factors determined, it is clear that the differences between the upper and lower edges of the band are real and of great importance. This is more clearly brought out in a subsequent chapter.

FIELDS ON THE DIAGRAM.

In plotting the coals different marks were used to distinguish the different types of the accepted classification—anthracite; semianthracite; semibituminous, bituminous, and subbituminous (all together); lignite; peat; woods; grains; and plants. On the diagram most of these fall into separate fields with little overlapping, the boundary lines between the fields being fairly sharp, in view of the fact that the different types are supposed to shade imperceptibly into each other. This is all the more remarkable when it is remembered that the classification of most of these samples has been determined by the field men more from the physical characteristics of the samples as they took them than from the analyses, and when the analyses were considered it was the proximate rather than the ultimate analysis that influenced their decision. Only in the case of the subbituminous coals and the lignites is there any serious overlapping, and this is easily explained by the fact that the early analyses by the United States Geological Survey and the Bureau of Mines were made at a time when it was customary to call the subbituminous coals the black lignites. Many of the "lignites" that seem from the diagram to belong in the subbituminous field were designated "black lignite" in the reports of the United States Geological Survey, or they at least have a low serial number, indicating that they were analyzed at the time when there was doubt as to their proper classification. Also, the oxidized or weathered subbituminous coals closely approach the lignites in composition, except for a scarcity of hydrogen.

For these reasons the diagram as obtained seems to be satisfactory as a method of classifying coals according to their ultimate analyses. The fact that the lines of division between the different fields do

^a The analyses were taken from the publications included in the bibliography presented herewith.

not cut perpendicularly across the band of dots, but as a rule are oblique, explains why the early work on the classification of coals from their ultimate analyses by use of such a ratio as that of carbon to oxygen failed to be accurate.

PLANT CONSTITUENTS IN COAL.

The cannel coals have a very disperse field, being high in hydrogen, and fall all along the upper side of the band out to a point where the fossil resins (see Pl. III, *B*) are found. This is interesting, if not suggestive. To be sure, much has been written on this subject, and it is not likely that the cannels are entirely composed of resins, but the possibility is suggested that some cannel coals at least could have resulted from the concentration of resin-bearing plant constituents, such as spore exines and cuticles, while in the peat bog. Thiesen and White^a have identified the resins and other constituents in coals with the microscope in all of the lower-grade coals and their derivatives in the higher-grade coals. A peculiarly satisfying check on their observations is found in that part of the band of coals where the curve bends toward the "100 per cent carbon" corner of the diagram. The quick turn in the band comes at a point that lies on a straight line between the carbon corner and the part of the diagram which contains the fossil resins. (See Pl. III, *B*.) From the principles explained in the exposition of the use of such a diagram one may assume that the original substances in the coal have decomposed at different rates, and that the resins and waxes are the most resistant to decomposition, so that as decomposition advances the composition of the coals should come nearer and nearer to that of the resins or to that of the products of decomposition of the more woody parts combined with the slightly altered resins. The coals that are nearest the part of the diagram containing the fossil resins should contain the greatest percentages of the resins or of their derivatives as compared to other coals, and this is true. The sudden bend in the coal curve on the diagram comes at the point of maximum concentration of the resinous derivatives as determined by Thiessen and White, and so it may be assumed that further change in the coal would have to be decomposition of the resins, and the line should bend away from the region of the resins. The diagram shows this to be true and confirms the results obtained by these microscopists and paleobotanists and their conclusion that the residues of resins can be found in the anthracites and semibituminous coals only with difficulty, but that these coals have doubtless once contained resins.

^a White, David, and Thiessen, Reinhardt, The origin of coal; with a chapter on the formation of peat, by C. A. Davis: Bull. 38, Bureau of Mines, 1913, 390 pp. White, David, Resins in Paleozoic plants and in coals of high rank: U. S. Geol. Survey Prof. Paper 85 E, 1914, 32 pp.

The regularity of the band, from the composition of woods and plants to the composition of pure graphite, with the characteristic break at the point where "anthracitization" sets in, and without a break to signify differences of origin of the different types of coal, likewise lends support to the theory that coals have been derived from plants that were chemically, at least, similar to those of the present age.

PRESSURE THE CHIEF CAUSE OF CHANGE IN COALS.

It is definitely known that many beds of coal have never been subjected to high temperatures and that the principal agency acting on them has been pressure. In fact, the coals that are known to have been heated have a certain marked composition that is different from that of the usual run of coals. The writer feels justified in assuming from the diagram that the change in composition of coals has taken place almost entirely through the agency of pressure. Critical examination of the data has revealed cases where, in a single bed of coal, parts have been subjected to stresses while other parts have been relatively undisturbed. In such a coal the analyses fall on the band farther and farther to the left as the stress has been greater, and as a rule the coals that are on the lower side of the band remain on that side of the band during further alteration, so that a material starting out on one side of the band is liable to remain in that position relative to the other coals as they are more and more metamorphosed. Tables of these analyses have been given in the publications of the Bureau of Mines and of the United States Geological Survey, and are readily accessible to anyone desirous of confirming the validity of these observations, but to incorporate them in such a paper as this would make it of too large a size. Suffice it to say, that numerous instances can be cited to show that a low-hydrogen peat tends to form a low-hydrogen series of coals and a high-hydrogen peat tends to form high-hydrogen coals. This is especially noticeable in the cannels.

One other important point is the direction in which the peats and vegetable debris decompose under pressure agencies. The line is not directly away from the point representing H_2O —it would be necessary for the peats to follow the "carbohydrate line" in such a case—but in such a direction that they must have lost some CO_2 and possibly CO as well. This would make them gain relatively in hydrogen, so that the residues would have more than enough hydrogen to form water with the oxygen present. This excess of hydrogen is what has been called "available hydrogen" by many coal chemists, and is used in a calculation of calorific values of coals

by Parr.^a The available hydrogen may be read directly from the diagram by subtracting the amount of hydrogen, as shown by the carbohydrate line, from the amount of hydrogen in the coal, the point used on the carbohydrate line being the point that indicates the same percentage of oxygen as the point representing the coal analysis. In other words, draw a line through the point representing the coal analysis parallel to the line of zero oxygen until it intersects the carbohydrate line. The excess of hydrogen in the coal over the amount of hydrogen at this point of intersection will be the available hydrogen.

It was said in the last paragraph that the decomposition of a coal by pressure tends to increase the available hydrogen, as shown by the diagram (Pl. I), up to the point in the band of coals where the sharp turn occurs and anthracitization sets in. It is a remarkable fact that the coking coals are concentrated around this region of maximum available hydrogen, as is pointed out in the section of this paper which has to do with the residues obtained by heating coals.

The indications are that the formation of anthracite, which sets in at this turn in the curve, seems also to be due to pressure alone, although the action of heat at this stage is apparently the same as that of pressure, as is pointed out later. Several sets of the analyses in Bulletin 22 that were plotted show points on the long branch of the curve, before the bend is reached, and other points, representing coal from the same bed, on the bend and on the anthracite section of the curve, although the geology of the region shows no intrusive sheets of lava, whereas the bed must have been much more deeply buried at one point than another if the heat of the earth's strata is to be credited with causing the differences in these coals. These facts tend to uphold the view that the average coal line, as plotted, is the "normal" line of change in coal substances as they grow older, and that pressure was the principal agent in the transformation.

Whether these inferences and deductions from the curve of coals are correct, the fact remains that the coals give a remarkably good band across the diagram; and classifying them by their position on the diagram, which, after all, is merely a method of expressing their total properties, seems to be productive of better results than any other method.

Some of the coals vary widely from the average line, and in the study of these "discrepancies" (which have really been the cause of the failure of all previous work to be comprehensive) some remarkable and useful facts have been revealed. The two most important relations that have been revealed are the differences in vola-

^a Parr, S. W., The available hydrogen of coal: Jour. Am. Chem. Soc., vol. 29, 1907, p. 582.

tile matter and calorific value between the coals on the upper and those on the lower side of the band. The differences between these quantities for the two sides of the band are so great that it is no wonder that the correlation of the ultimate analysis with the proximate analysis, beyond some broad and nonmathematical qualitative statements, has been deemed impossible. The results here plotted are hence probably the first definite connection that has been established. They show that not only the physical properties of a coal, which determine its classification, but also some of the inner chemical properties, as shown by the percentages of volatile matter and calorific value, are definite functions of the ultimate analysis of the coal.

RELATION OF CALORIFIC VALUE TO ULTIMATE ANALYSIS.

The relation between the calorific value of the coals plotted and the ultimate analysis was determined by drawing through the points lines which connect coals of equal calorific value (Pl. II, *A*), the composition of the coals being computed in terms of carbon, hydrogen, and oxygen, and a correction of the calorific value being applied for sulphur. Such lines might be called "isocalorific lines" or "isocal." The lines overlapped considerably if the number of calories between isocal was small, but by choosing values far enough apart and plotting only the lines representing the averages of these points, smooth curves that were nearly parallel throughout their length were obtained.

PROBABLE ERRORS IN PLOTTING.

A serious question arises at this point as to whether the variations between the isocalorific lines (which have been so spaced that none of the variations falls beyond the next isocal) are the result of accident, or whether these variations are small but real. In order to answer this it is necessary to consider the probable errors of each quantity determined in the analysis. Data on this point were obtained from A. C. Fieldner, chemist of the Bureau of Mines. He gave as the probable errors in analyses of coal the following set of figures:

TABLE 1.—*Probable errors in analysis of coal.*

Determination.	Range.	Probable error.	Determination.	Range.	Probable error.
	<i>Per cent.</i>	<i>Per cent.</i>		<i>Per cent.</i>	<i>Per cent.</i>
Moisture.....	0 to 5	± 0.1	Volatile matter.....		± 0.3
Do.....	5 to 10	± 0.15	Volatile matter by modified		
Do.....	10 to 15	± 0.20	method.....		± 0.5
Ash.....	0 to 25	± 0.1	Nitrogen.....		± 0.04
Ash in presence of carbonates.....		± 0.2	Carbon.....		± 0.3
Sulphur.....	0 to 2	± 0.04	Hydrogen.....		± 0.05
Do.....	2 to 4	± 0.07			<i>Calories.</i>
Do.....	4 to 6	± 0.10	Calorific value.....		± 20.0

As the ordinates for oxygen are almost perpendicular to the isocaloric lines, a good way to test the effect of experimental error on the locus of a point, and hence its position on or off of its proper isocal, is to determine the probable error of the oxygen determination, as conditioned by all the other factors, from which the oxygen is calculated, each of which is subject to a probable error. In the ordinary method of analyzing coals after every other constituent has been determined, the residue is called "oxygen," and hence all of the error of the work falls on the oxygen. Using the ordinary formulas for the probable error of a single determination of a quantity that is dependent on the sum or differences of two or more other quantities, each subject to definite probable errors, and using the values given in Table 1, the probable error of the oxygen determination for a single analysis is ± 0.633 per cent. This figure would have to be modified to allow for some of the divisions that are performed in the further calculation of the "pure-coal" oxygen, but were disregarded here as being of small relative effect upon the total probable error, though they would tend to increase it. The value ± 0.633 per cent as the probable variation of the oxygen percentage on either side is close enough for the purposes of this discussion, and it is interesting to see how nearly this covers the facts.

The accuracy of the calorific determination has permitted of isocals being drawn closer together for the higher-grade coals than for the lower-grade coals. This accords with the difficulty of getting good results on the moisture, ash, and volatile matter in analyzing the lower coals. As to the average distance between the isocals for the average bituminous coals, for which the probable oxygen error is assumed to be ± 0.633 per cent, the diagram shows them to be a distance apart corresponding to about 2 per cent of oxygen, as measured on a perpendicular to the "zero-oxygen" line, whereas the probable variation of ± 20 calories, or ± 36 B. t. u., corresponds to about ± 0.2 per cent oxygen. If the probable error of placing the point as expressed in terms of percentage of oxygen is combined with the probable error of the calorific value, as expressed in terms of oxygen coordinates of the two points on the diagram that show a composition corresponding to the erroneous calorific values, the combined probable variation of the oxygen ordinate is ± 0.663 per cent. The actual distance apart of the isocals, as determined roughly with the guiding criterion of making most of the errors fall between the correct isocal and the next one, being about 2 per cent, which corresponds to $+1$ or -1 per cent as measured on the oxygen ordinate at the most, is thus seen to be in good agreement with the probable error of the whole work. However, the probable error does not represent the maximum possible error, and the determination of the interisocal distance that would allow most of the

errors to fall between the correct isocal and the next one is unavoidably influenced by the maximum errors, which assume too much importance when matters of personal judgment are allowed to have weight, as was the case in spacing the isocals.

More rigorous treatment of the errors would involve a more extended mathematical explanation than would be warranted in this paper, though it would doubtless be of scientific value. The writer believes that the close agreement of the variations of calorific value from the isocalorific lines with the roughly calculated probable variations is sufficiently satisfactory.

It is not hard to find coals that vary more or less widely from these isocalorific lines, but the analyses, almost without exception, show the coals to be high in sulphur, ash, moisture, or some other disturbing factor that would naturally tend to leave the results in greater error. If coal were a pure substance, such as has been used in the careful thermochemical work of many experimenters in organic chemistry, it might be possible to draw much finer distinctions between the different grades of material, but the variation between the calorific values of pure organic compounds that happen to be isomers is of nowhere near the same magnitude as the probable errors of placement of the points on the diagram, and so even if two coals were isomeric in composition and yet different in inner structure, the difference in calorific value would not be discernible from this diagram.

However, the calorific value of coal seems to be a definite function of the ultimate analysis within, or very close to, the limits of the total errors of analysis. This result has been reached entirely by empirical methods, and hence has nothing to do with the various formulas that have been devised to calculate the calorific value of a coal from the ultimate analysis. The graphic treatment of the problem has merely shown that the calorific value is a function of the ultimate analysis, without determining what that function is—and it may be highly complicated—because the fact that isocalorific curves may be drawn is enough to show that the relation does exist. It might be possible to find a formula that would adequately represent in algebraic language what is pictured in the diagram, but this would necessarily be difficult, and the diagram is compact enough for all of the information that it contains without needing to resort to formulas. It is possible that the close parallelism of the isocals may make the problem of deriving an algebraic function to fit them a simple matter. As even this function would be empirical and certainly subject to some variation from the plotted curves which are already enough in error no attempt will here be made to give a formula that might lead to erroneous conclusions. However, the use

of the calorific diagram for further studies of this kind and for comparison with the calculated calorific value by such a formula as that of Dulong seems promising.

Porter and Ovitz,^a in investigating the volatile matter from various types of coal, found that the oxygen of the lower grades of bituminous and subbituminous coals tended to combine as CO_2 and CO to a greater extent than in the higher-grade coals, the increase in these compounds taking place at the expense of the H_2O formed. That is to say, the oxygen of the coal tended to form oxides of carbon rather than water, and it is also a well-known fact that these coals give higher calorific values than are called for by Dulong's formula. This seems to uphold the hypothesis that the increase in oxides of carbon evolved has made a still greater amount of "available hydrogen" within the coal which gives the greater calorific value. At least, Porter and Ovitz give modifications of Dulong's formula to apply to the lower grades of bituminous and subbituminous coal that fit the facts more closely. By means of a diagram, such as Plate II A, it should be possible to work out a whole series of corrections for Dulong's formula, and possibly incorporate them all into one function to be applied with Dulong's equation. This might be done by first plotting the isocals as determined by calculation from Dulong's equation and then finding what factor would be necessary to make such a curve coincide with the observed isocal. As mentioned above, the writer can see little profit in going any farther into the realm of the empirical, though a set of correction factors might be evolved for sulphur that could be applied directly to the diagram. This feature could doubtless be made the basis of an interesting study of the thermochemical aspect of coal from a purely scientific aspect.

RELATION OF VOLATILE MATTER TO ULTIMATE ANALYSIS.

A study of the same coals for a relation between volatile matter, calculated to an ash and moisture free basis, and the ultimate analysis has likewise resulted in a seeming relation, and it has also been possible to draw curves through the points of equal volatile-matter content yielding a set of "isovolatile" lines or "isovols" (Pl. II, B). The isovols are not straight lines, nor do they even approximate a straight line, as the isocalorific lines seem to do. Moreover, they had to be taken farther apart in order to find any relation. That is to say, the errors of determination are much greater. By the process of reasoning employed for the calorific values the error of placement of the point on the isovol diagram due to errors in the analysis is the same as for the isocal diagram, but errors in the volatile-matter determination are of much greater relative magnitude than those in the calorific-

^a Porter, H. C., and Ovitz, F. K., The volatile matter of coal: Bull. 1, Bureau of Mines, 1910, pp. 42-44.

value determination. Moreover, the "volatile matter" is subject to large constant errors that are superposed on the probable errors. The constant errors are due to factors, such as sulphur content. The sulphur of coal often is in the form of pyrite, which on being heated away from air loses part of its sulphur. Moreover, the presence of calcium carbonate causes error in the volatile matter, owing to the loss of CO_2 on heating. Instances might be multiplied, and anyone familiar with coal analysis will wonder that there should be any relation at all between the volatile matter and the ultimate analysis, in view of all the disturbing factors.

The complete treatment of the subject of the errors of volatile-matter values would hence fill more space than is necessary in this report. However, a fairly close relation can be found, as has been shown in Plate II, *B*. The coals on the upper side of the band (Pl. I) differ greatly from those on the lower side, and it is possible to have two coals of almost identical ultimate analysis except for a slight difference in their hydrogen content, which makes a great difference in the amount of volatile matter. This may help explain why many chemists have felt that it was impossible to find any connection between the ultimate analysis and the volatile matter. The fact that the hydrogen in coal can be determined with greater accuracy than almost any other constituent would encourage the use of that factor as a criterion of the volatile-matter content.

Again, the relation seems to hold fairly well when the ash, sulphur, and other disturbing factors are low, and presumably the variations of the volatile matter for coals high in ash are due to insufficient data as to the disturbing factors.

The fixed carbon should give a diagram similar to the isovolatile diagram and with the lines slanting the same way with respect to the base. Nothing would be gained by making a fixed-carbon diagram, however, as the sum of the volatile matter and the fixed carbon is 100 per cent, and the diagram for volatile matter should be sufficient for purposes of defining the system.

Doubtless a better agreement could be obtained by plotting a volatile-matter diagram of the coals from one seam only, as supposedly they are much more closely related than are the coals here plotted, which represent coals from all over the United States. Such a diagram for each mining district should be of practical use in conjunction with the other diagrams here developed, and in the shape of a wall map could be continually referred to with profit.

COMBINING TWO SETS OF CURVES ON ONE DIAGRAM.

The diagrams of calorific value (Pl. II, *A*) and volatile matter (Pl. II, *B*) are combined as a single diagram in Plate II, *C*. The isocals and the isovols slope in opposite directions, and hence can

not be confused with each other. Moreover, the combination has the added advantage that from the two determinations of volatile matter and calorific value the inquirer can work back to get an idea of the ultimate analysis, and from that an idea of the other properties of the coal in question. The method of doing this is very simple. The point representing the results of an ultimate analysis must lie on one of the isovols, which may be found from the volatile-matter determination, and also on a certain isocal, which may be found from the calorific value, and crosses the isoval, and hence the required point is the point of intersection of the isovol and isocal. As an example, there is only one ultimate analysis on the diagram which corresponds to 40 per cent volatile matter and a calorific value of 13,000 B. t. u.

Similar useful combinations might be made of other pairs of diagrams which could be developed. The method is an old one and has been widely used in determining the analysis of ternary systems of elements or compounds from any pair of physical properties of the combination.

RELATIONS OF MOISTURE, ASH, SULPHUR, AND NITROGEN TO THE ULTIMATE ANALYSIS.

MOISTURE.

Recent investigation by the Bureau of Mines, the results of which are given in Technical Paper 113,^a has shown that different coals have each a definite partial pressure of water vapor for a given moisture content, and that the total vapor pressure varies in different coals with the same moisture content. Each coal should show a characteristic moisture determination if it has been air-dried in air of constant humidity. Unfortunately such procedure is not usual in the determination of moisture. Coals are dried for analysis in a constant-temperature cupboard, but the humidity of the air passed over them varies from day to day, so that they are not at the same relative starting point when moisture is determined. On this account the published moisture determinations are found to be of little more than qualitative value when an attempt is made to draw curves of equal moisture content across the diagram. All that can be said is that the higher a coal is in oxygen, the higher it is in moisture content; that is, the moisture curves would slope in the same general direction as the isocals.

ASH, SULPHUR, AND NITROGEN.

Ash, sulphur, and nitrogen are not found to vary according to any known laws, and it would be exceedingly surprising if the first

^a Porter, H. C., and Ralston, O. C., Some properties of water in coal: Tech. Paper 113, Bureau of Mines, 1915.

two did. The ash may be regarded as a purely accidental constituent, as most of it is manifestly from the mud and sands that buried the coals when they were in the peat-bog stage. Of course some of the ash comes from the original ash of the plants, but even that is not in constant proportion. A possible relation might exist between the sulphur content and the ultimate analysis as most of the sulphur is in the form of pyrite that has been precipitated in the coal after the beds were buried, and it could be possible that the pyrite replaced certain definite parts of the coal. If this is so, however, it can not be detected by present methods.

About the only feature that seems to be general is that many of the coals high in sulphur are also high in hydrogen and volatile matter. This point has merely been observed in the study of the coals with regard to other constituents, and it did not hold for all analyses, but still was prominent enough to attract the writer's attention. Until it has been further verified there is no use in theorizing about it.

The proportion of nitrogen, as has been remarked by many writers, is fairly constant and never varies much from 1.25 per cent, although it may be as high as 2 per cent or as low as 0.5 per cent. In this investigation no very great study of nitrogen in coals was made, but the indications are that it does not vary in any manner that can be formulated. As shown by the table of probable errors, it is possible to get close checks in determining the nitrogen content, but as to the constant errors that are incorporated under the term "nitrogen" little is known, except that they are rather large. Until further work has been done on the question of determining the nitrogen in coals it is not likely that any relation of nitrogen to other properties of the coal will be discovered. All that is known is that nitrogen must be a constituent of some parts of the coal, most probably the humus derivatives.

RESIDUES FROM THE HEATING OF COALS.

In investigating the causes of the wide variations of a few of the coals from the average line of coals, as revealed by Plate I, it was found that the coals that had been heated were somewhat different from the unheated coal, and that the differences seemed to be based on certain definite tendencies. The data on the subject are from many sources, and if all were plotted on one diagram would make it too complex. Only illustrative analyses are therefore given, and anyone wishing to test the matter further is referred to the literature on the subject as contained in the bibliography at the end of this paper. The results of some experiments by others on heating coals and woods are given in Table 2.

TABLE 2.—Solid residues from the heating of coals, woods, etc.

No. of sample. ^a	Composition.		Description of material and conditions of treatment.	Authority.
	Carbon.	Hydrogen.		
	<i>Per cent.</i>	<i>Per cent.</i>		
1.....	51.10	6.16	Wood, unaltered sample.....	Stein and Brislee.
2.....	63.53	5.53	Wood, sealed in glass, with H ₂ O, heated for 9 hours, at 245° C.	Do.
3.....	69.18	5.12	Wood, sealed in glass, with H ₂ O, heated for 9 hours, at 250° C.	Do.
4.....	70.57	4.94	Wood, sealed in glass, with H ₂ O, heated for 6 hours, at 255° C.	Do.
5.....	72.77	4.73	Wood, sealed in glass, with H ₂ O, heated for 5 hours, at 265° C.	Do.
6.....	74.03	4.52	Wood, sealed in glass, with H ₂ O, heated for 5 hours, at 275° C.	Do.
7.....	77.58	4.12	Wood, sealed in glass, with H ₂ O, heated for 5 hours, at 280° C.	Do.
8.....	81.30	3.82	Wood, sealed in glass, with H ₂ O, heated for 5 hours, at 290° C.	Do.
9.....	83.93	2.73	Charcoal.....	Do.
10.....	97.94	0.51	do.....	Do.
11.....	80.93	6.70	Coal, unaltered sample.....	Wright and Brislee.
12.....	95.89	2.07	Same, heated to 800° C.....	Do.
13.....	96.76	1.17	Same, heated to 1,100° C.....	Do.
14.....	87.60	5.12	Coal, unaltered sample.....	Lewes.
15.....	89.69	4.15	Same, coked, at 450° C.....	Do.
16.....	77.10	4.18	Wyoming coal, near outcrop.....	Bureau of Mines.
17.....	87.02	2.03	Wyoming coal, heated by burning outcrop.....	Do.
18.....	52.4	5.50	Peat, unaltered sample.....	Bergius.
19.....	74.3	5.20	Same, heated under pressure for 8 hours, at 250° C.	Do.
20.....	77.0	5.00	Same, heated under pressure for 8 hours, at 300° C.	Do.
21.....	81.2	4.64	Same, heated under pressure for 8 hours, at 340° C.	Do.
22.....	84.0	4.62	Same, heated under pressure for 24 hours, at 340° C.	Do.
23.....	85.2	4.50	Same, heated under pressure for 61 hours, at 340° C.	Do.
24.....	44.35	6.28	Cellulose, unaltered sample.....	Do.
25.....	83.7	5.40	Same, heated under pressure for 64 hours, at 310° C.	Do.
26.....	83.1	5.20	Same, heated under pressure for 8 hours, at 340° C.	Do.

^a Same as in Plate III, A.

EFFECT OF HEATING AT ATMOSPHERIC PRESSURE.

The most characteristic thing about the pyrogenetic decomposition of these solid fuels is that if the distillation is carried on at atmospheric pressure, or at pressures less than atmospheric, the alteration in composition of the residue is represented by a straight line that points almost straight toward the carbon corner of the diagram (Pl. III, A). The more highly the material is heated and the longer it is heated the more it alters and the closer it approaches in composition to pure carbon, though it will be seen that most of the charcoals and cokes are far from being pure carbon. As a matter of fact, the tendency of carbon to hold back oxygen has been noticed by Langmuir^a at temperatures as high as 1,200° and even 1,500° C. The time as well as the temperature seems to have an effect on how far the coal has altered toward pure carbon.

A natural consequence of the tendency of coal when heated to alter to carbon is for the residue to be lower in percentage of hydrogen than the normal coal having the same percentage of carbon. It is this

^a Langmuir, Irving, Chemical reactions at very low pressures: Jour. Am. Chem. Soc., vol. 35, 1913, pp. 931-945.

property that makes the point representing the analysis of the coal on the diagram fall in a rather unusual position. Nearly all of the coal analyses that were given in Bulletin 22^a as having been heated were found to be low in hydrogen, and it was often found in looking up the data on a coal analysis that seemed to be rather unusual that the sample was from a bed that lay near intrusive sheets of lava, or that it was from a place near which the outcrop of the bed had burned. Such coals are common in Wyoming, Montana, and Colorado. This fact is extremely useful, as it enables one from the analysis of a coal that has been heated to calculate by extrapolation the probable composition of the coal from which it came. For example, the points representing the so-called graphitic anthracites of Rhode Island are almost on a straight line between the points representing the normal Triassic coals, as found in other places, and the "100 per cent carbon" corner. This fact may be an aid in the question of the low-temperature coking of fuels, and also in other problems. The points representing the volatile matter and calorific value of these low-hydrogen coals fall in line with the isovals and isocals, respectively, that were drawn for the normal coals, so that these lines can be extended to cover more of the diagram than they would otherwise do.

EFFECT OF HEATING UNDER HIGH PRESSURE.

If the coal is heated in a confined space under pressure, the line of decomposition does not point straight toward the carbon corner, but has a flatter slope, the residues being relatively higher in hydrogen. The best examples of this are in the heating of woods and peats that are given in Table 2. The data there attributed to Bergius^b were obtained under some of the highest pressures of the examples given, a pressure of several thousand atmospheres being attained in some cases. The application of pressure to a fuel under distillation seems to hinder the reaction of pyrogenetic decomposition and to increase the reaction due to pressure, so that the higher the pressure the flatter the slope of the decomposition line. Two physicochemical principles uphold this conjecture. The pressure tends to retard the heat reaction because the products of decomposition are not allowed to escape, and, as is well known, by their presence tend to retard the reaction. Likewise the increase in rapidity of chemical reaction with temperature would tend to hasten the pressure reaction so that it might preponderate over the temperature reaction. Therefore the higher the

^a Lord, N. W., *Analyses of coals in the United States, with descriptions of mine and field samples collected between July 1, 1904, and July 30, 1910, with chapters by J. A. Holmes, F. M. Stanton, A. C. Fieldner, and Samuel Sanford*: Bull. 22, Bureau of Mines, 1913, 1200 pp. In two parts.

^b Bergius, F., *Production of hydrogen from water and coal from cellulose at high temperatures and pressures*: Jour. Soc. Chem. Ind., vol. 32, 1913, p. 462.

pressure the nearer will the line of decomposition follow a direction that coincides with the line of "coalification," and hence the flatter will be its slope. It is possible that the careful study of this question of pressure would reveal a definite relation between the slope of the line of decomposition and the pressure, and hence give an opportunity of applying the diagram to the study of such problems as the pressures under which various coals have been heated when intruded by a lava bed—at least many interesting and seemingly profitable lines of research are opened up. The results as here stated are based on data by different chemists working on slightly different products, and hence should not be used for rigid calculation, but serve to point out the general nature of the phenomena to be expected. No single person has carried out a research on one substance that covers all of the factors mentioned, and it would be most interesting to see if what has been said holds rigidly true, and also to try to place the results in mathematical form.

COKING COALS.

The subject of the coking of coal naturally finds a place in this section of the paper. In the diagram (Pl. III, *A*) are represented the coking coals that have been analyzed by the Bureau of Mines and that are definitely known to be coking coals. Many other coals of which the analyses have been published by the bureau may have the property of coking, but unless it has been definitely stated that they are used for coke they are not included in Plate III, *A*. The coking coals are represented in the illustration by dots. Most of them lie near the sharp bend in the average coal curve at the point where their resinous contents are supposedly a maximum, and those that are not near this bend, which means that they are lower in carbon, are as a rule quite high in hydrogen, which also indicates a high resinous content. From what was said under the section on classification and from these facts it would seem that the coking quality of coals is expressed in the ultimate analysis by lying in a certain field of the diagram which represents a high resinous content. (See Pl. III, *B*.) The argument is further strengthened by the work of several chemists^a who have extracted coals with different solvents and are able to remove, by means of caustic-alkali solutions or pyridine or chloroform or the like, a resinous extract that is high in hydrogen and will coke; and leave a residue that is low in hydrogen, will not coke, and seems to consist of the derivatives of the "humus" compounds that entered the coal. Whether the theory that resinous substances impart the coking property to coal is true or not, the fact

^a See discussion of the work of Baker, Anderson, Lewes, and others by Lewes, V. B., *Carbonization of coal*, 1912, p. 17.

is that the coking coals fall in a position that tends to uphold such a theory. The analyses of several representative cokes are also plotted in Plate III, *A*, although it is somewhat doubtful if the ultimate analyses of such products mean anything, for the reason that they do not yield up their nitrogen, etc., very well on analysis. But they are doubtless near enough for the purpose of this discussion in showing the general direction in which the coking coals decompose; the low-temperature cokes in especial show this. Further discussion of the coking properties of coal are to be found in other bulletins and papers of the Bureau of Mines and the Geological Survey (see Bibliography), but it might be well to call attention to the agreement of the results shown in Plate III, *A*, with other criteria as to the coking quality of coals.

HYDROGEN AS AN INDEX TO COKING QUALITY.

Parr^a has taken the "available hydrogen" as an index of the coking quality of coal and one can see from the position of the dots on the diagram, being high above the carbohydrate line and in a direction parallel to the oxygen zero line, that the coals known to be coking are the highest in available hydrogen.

Another criterion for the coking quality of a coal is the ratio of hydrogen to oxygen, as used by White.^b The highest ratio of hydrogen to oxygen is found in the coking coals. In the triangular diagram the ratio of hydrogen to oxygen is represented by the proportions in which a line parallel to the zero line of carbon and drawn through the point representing the coal is divided by the point. If a line be drawn from the carbon corner through the point representing the coal and produced till it intersects the line of zero carbon it will be found that this intercept is highest for the coals having the highest hydrogen-oxygen ratio. Again it is the coking coals that show the highest hydrogen-oxygen ratio on the diagram, a result which agrees with White's conclusions.

Although the agreement with the work of others is very good it would not be hard to pick out on the diagram points with relatively high available hydrogen or hydrogen-oxygen ratio—perhaps just as high as that of some coals that are known to coke—and yet in such a position on the diagram that one may assume that they very probably do not coke and find the assumption borne out by statements to that effect in the description of the samples. The advantage of the graphic method is that the coking coals are in a definite field and coals outside of this field will not coke, whereas it

^a Parr, S. W., The available hydrogen of coal: *Jour. Am. Chem. Soc.*, vol. 29, 1907, p. 582.

^b White, David, The effect of oxygen in coal: *Bull. 29, Bureau of Mines*, 1911, 74 pp. Reprint of U. S. Geol. Survey Bull. 382.

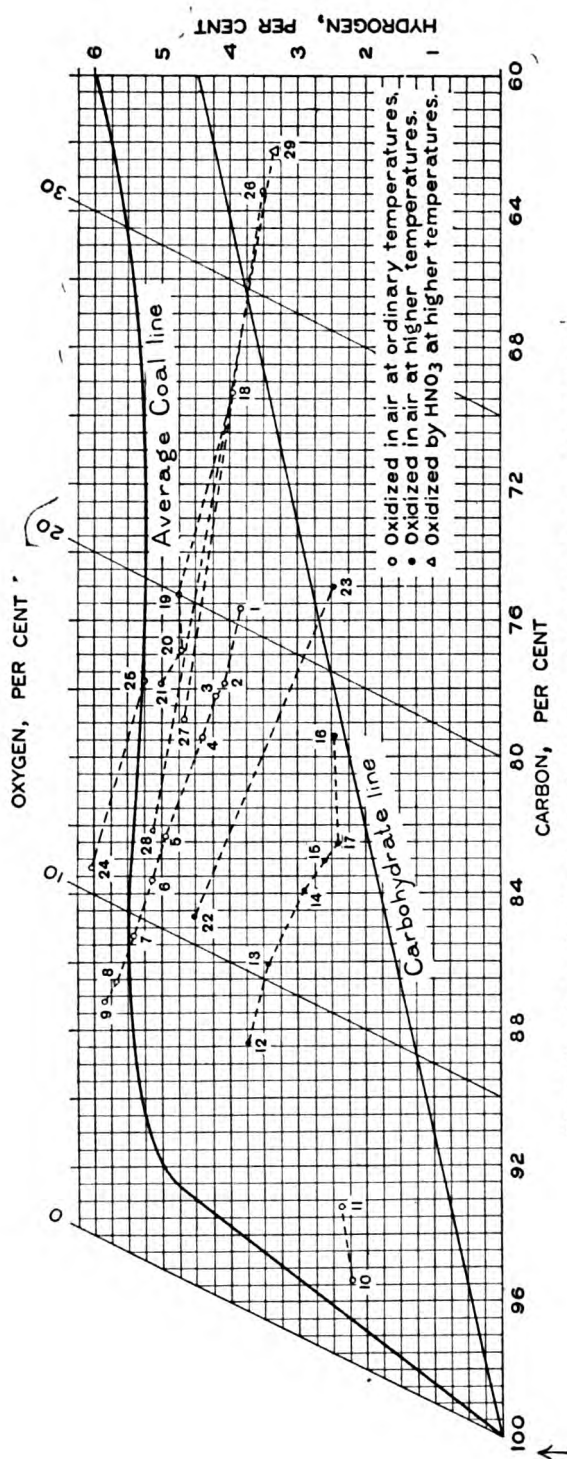


FIGURE 6.—Curves showing results of oxidation. Numbers are same as in Table 3.

is hard to find coals in it that will not coke. It is because the division lines between the coals of equal available hydrogen and hydrogen-oxygen ratio do not happen to coincide with the boundaries of the field of coking coals that these other criteria sometimes fail.

SUMMARY.

The application of the diagram to the study of the residues from the heating of the solid fuels is singularly fruitful and opens up great possibilities of coordinating data in the mapping out of the paths of decomposition of various coals, as well as determining the conditions for obtaining cokes of different qualities, and with varying amounts of volatile matter and with differing calorific values.

RESIDUES FROM THE OXIDATION OF COALS.

Another set of points that show apparently large variations from the average analysis are the coals that had been oxidized in one manner or another. The direct addition of oxygen to a coal would naturally tend to make the total composition of the combination change toward the direction of the oxygen corner. This is illustrated by figure 6, which was constructed from the data given in Table 3.

TABLE 3.—Composition of oxidized coals.

No. of sample. ^a	Composition.			Description of sample and conditions of test.	Authority.
	Carbon.	Hydrogen.	Oxygen.		
	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>		
1.....	75.66	3.84	20.50	Bituminous coal, Experimental mine, outcrop.	Porter and Fieldner.
2.....	77.83	4.07	18.10	Same, 1 foot in from outcrop.....	Do.
3.....	78.17	4.22	17.61	Same, 5 feet in from outcrop.....	Do.
4.....	79.30	4.39	16.31	Same, 10 feet in from outcrop.....	Do.
5.....	82.37	4.96	12.67	Same, 20 feet in from outcrop.....	Do.
6.....	83.61	5.15	11.24	Same, 25 feet in from outcrop.....	Do.
7.....	85.25	5.42	9.33	Same, 35 feet in from outcrop.....	Do.
8.....	86.56	5.68	7.76	Same, 55 feet in from outcrop.....	Do.
9.....	87.18	5.85	6.97	Same, 125 feet in from outcrop.....	Do.
10.....	95.37	2.20	2.43	Pennsylvania anthracite in 1890, fresh.	Mahler.
11.....	93.19	2.37	4.44	Same anthracite in 1910, kept in laboratory air.	Do.
12.....	88.39	3.74	7.87	Bituminous coal, as collected.....	Do.
13.....	86.03	3.43	10.54	Same, in air at 100° C.....	Do.
14.....	83.90	2.90	13.20	Same, in air at 150° C.....	Do.
15.....	83.02	2.60	14.38	Same, in air at 200° C.....	Do.
16.....	79.37	2.45	18.18	Same, in air at 250° C.....	Do.
17.....	82.51	2.40	15.09	Same, in air at 300° C.....	Do.
18.....	69.33	3.98	26.69	Subbituminous coal, Almond, Wyo., 50 feet in mine.....	United States Geological Survey.
19.....	75.23	4.77	20.00	Same, 150 feet in mine.....	Do.
20.....	76.86	4.72	18.42	Same, 575 feet in mine.....	Do.
21.....	77.72	5.02	17.26	Same, 1,000 feet in mine.....	Do.
22.....	84.66	4.51	10.33	Bituminous coal, as collected.....	Richters.
23.....	75.00	2.46	22.54	Same, in air at 190° C.....	Do.
24.....	83.24	6.04	10.72	Bayne, Wash., bituminous coal, fresh.	Bureau of Mines.
25.....	77.73	5.26	17.01	Same, outcrop.....	Do.
26.....	69.39	3.51	27.10	Buckey, Mont., subbituminous coal, weathered.	Do.
27.....	78.87	4.68	16.45	Same, but slightly altered.....	Do.
28.....	82.17	5.15	12.68	Scotch coal, as collected.....	Anderson.
29.....	62.25	3.35	34.40	Same, treated with nitric acid.....	Do.

^a Same as in figure 11.

Very few of the coals that have been oxidized have been altered in composition in a line directly toward the oxygen corner, but have been altered more nearly toward the point that represents CO_2 . The reason must lie in the fact that the complex of coal and oxygen breaks up to some extent, so that all of the added oxygen does not remain fixed but some of it escapes as H_2O , CO_2 , and CO .^a The actual path of the composition of the oxidizing coal will be a resultant of these two tendencies, (1) a direct addition of oxygen, and (2) a partial splitting up of this complex. It could therefore hardly be expected that the lines of alteration of different coals should all point to the oxygen corner and they do not, but are more nearly parallel to each other when the coals are treated under like conditions. Why they are so nearly parallel the writer does not venture to say.

This alteration will leave the residue lower in hydrogen than the average coal, and the greater the oxidation the greater will be the deficiency in hydrogen, and except for the deficiency in hydrogen the coal will be very close in analysis to a much lower-grade coal. (See the altered subbituminous coals, Pl. III, *B*, Nos. 18, 19, 20, and 21, which closely resemble lignite in composition.) Knowing the average direction of this change it is then possible by extrapolation to find in the normal or average band the coal that had probably been altered to produce the coal in question. Applications of this principle by comparing the analysis of weathered coal from the outcrop of a bed with that of the unweathered coal farther in have been singularly successful, and there is plenty of data in Bulletin 22 to check this assertion.

The ordinary methods by which samples of coals may be oxidized are by long weathering in air, oxidation with chemicals in the laboratory, or heating in air or oxygen. Examples of all of these are given in figure 6. Again, the amount of data available is so great that most of it is left out in order to gain simplicity in the diagram.

A comparison of the coals that have been oxidized at higher temperatures than atmospheric with the weathered coals shows that their oxidation curves have a steeper inclination and if prolonged would not pass as near the oxygen corner, which means that their coal-oxygen complex has been more thoroughly broken up, or else it means that superposed on the oxidation effect has been a heat or distillation effect, which, of course, has a curve that slants to the left instead of to the right. It is possible that both oxidation and distillation enter in, and it is evident that the actual direction of change is the resultant of an extremely complicated combination of factors. Attention is again called to the possibilities of research on the oxidation of coals with this sort of a diagram as a guide.

^a Porter, H. C., and Ralston, O. C., A study of the oxidation of coal: Technical Paper 65, Bureau of Mines, 1914, 30 pp.

COAL CONSTITUENTS, FRACTIONS, AND RESIDUES.

The analyses of many of the substances that are known to go into coal, or have been removed from coal, either by fractional distillation or solution, are plotted in Plate III, *B*. The plate shows clearly the constituents that may be expected in coal. The woods, grains, and such products were included in Plate I and are not plotted here. The resins also carbonize to some extent, so that the fossil resins are somewhat nearer the carbon corner than the fresh ones, but, like coals, the change has increased the available hydrogen. The fats and waxes and asphalts are somewhat higher in hydrogen than the resins, hence their higher calorific power. The different kinds of tars—pitch, coal tar, cellulose tar, starch tar, and sugar tar—form a fairly regular series, and it is to be regretted that the ultimate analyses of tar as it is distilled from the coals has not received more attention. The various gases obtained are not represented.

Hoffman and Frazer^a have dissolved various products from coal with phenol as a solvent and then fractionated the soluble extract, getting the fractions of the analysis represented by the triangular dots. What these constituents are is hard to say, but further work is being done.

Analyses from Bulletin 22 were also tabulated to determine the difference between the different parts or benches of a bed of coal, such as the top, middle, and lower benches. There was no uniformity in the differences found and so the results are not plotted here. About the only feature that seemed to be of frequent occurrence was that the top layers of a bed were higher in hydrogen than the lower. This might have been caused by the resins and waxes tending to float in the old peat bogs and coincides somewhat with the observation that the cannel streaks so often found in some beds generally occur near the top of the bed. However, the phenomenon is far from being general. An effort was also made to compare the analyses of different screen sizes of sample lots of coal as reported in Bulletin 22. The results were almost entirely negative, as some slack coals were higher in hydrogen or carbon than the lump and some were lower.

OTHER APPLICATIONS OF TERNARY DIAGRAM.

Other properties of the coals that could be studied in this manner and a diagram made which could be used for tabulating the results, if nothing else, are the iodine number and other index numbers of organic chemistry, the KMnO_4 number, the rate of oxidizability, and the inflammability. Such a diagram might be of value in commercial practice for predicting the amounts and analyses of the

^a Hoffman, J. C. W., and Frazer, E. F., Constituents of coal soluble in phenol: Tech. Paper 5, Bureau of Mines, 1912, 20 pp.

gases that could be distilled from a fuel of given composition. The procedure for doing this on a three-component gas has been worked out, but there seems to be no way of solving for more than three constituents, whereas the gas as a rule contains many different constituents. Therefore the gas diagram is not given here.

For a study of any one, two, or three of the gases that are liberated on heating fuels, such a diagram should prove useful, but the published data are far from being comparable and further research is necessary to develop a diagram that will have a general application. The gas manufacturer, in particular, should be able to work out diagrams of great value to his work and thus tabulate the masses of data he must use.

This method might be applied in the study of oils and fats, rubber, wood, etc. In any case where the molecular weights or other molecular properties of the substances being examined are not known, or where they are complex mixtures of substances too complicated to treat in the ordinary fashion, this type of diagram should prove useful. There are many such cases in applied organic chemistry—the ones mentioned are the most evident.

SUMMARY.

1. The ordinary type of trilinear coordinates can be applied to the study of complex systems made up of three elements, such as coal, wood, etc.

2. A modification of the ordinary type of trilinear coordinates allows the plotting of three component systems on any triangle as a base and automatically compensates for the differences in the errors of determination of the different components.

3. The plotting of all the coal analyses available, considered as "pure coal" (carbon, hydrogen, and oxygen), on an ash, moisture, nitrogen, and sulphur free basis, on such a diagram reveals the fact that the various grades of coal of the accepted classification fall into definite fields on the diagram.

4. From the direction of evident change in composition of coals with age it is possible to draw many deductions that agree with the experimental work of others.

5. Connecting the points representing coals of equal calorific value and those of coals having equal volatile matter gives a series of lines, called "isocals" and "isovols," respectively, which plainly show a relation between the ultimate analysis and each of these two entities. Considerations of the probable errors in the determinations, of the plotting of the points representing the coal analyses, and of these two entities, show that the errors in plotting are probably within the total experimental errors to be encountered. A combination diagram, with the isocals and isovols crossing each other,

shows the possibility of predicting the ultimate analysis from a knowledge of the calorific value and the volatile matter of a sample of coal, or vice versa.

6. The author discusses the possibility of applying the same method to the representation of the moisture in coal, and points out the hopelessness of looking for a relation between the ultimate analysis and either the ash, sulphur, or nitrogen.

7. The ternary diagram may be applied to a study of the residues from the heating of coals, etc., and to studying the problem of distillation of fuels and coking. Several new facts have been observed as to the relation of pressure, heat, and time to the analysis of the residue from heating a coal.

8. An application of the diagram to the study of the oxidation and weathering of fuels results in valuable conclusions.

LITERATURE CONSULTED.

Following is a list of some of the publications consulted by the writer in preparing this paper, including those mentioned in the text:

ANDERSON, W. C. A contribution to the chemistry of coal, with special reference to the coals in the Clyde Basin. *Proc. Phil. Soc., Glasgow*, vol. 29, 1897, pp. 72-96.

BANTLING, GERHARD. Pyrogene Zersetzung von Zellulose, Stärke, Zucker, und Sulfitzelluloseablauge. *Jour. Gasbel., Jahrg.* 57, 1914, pp. 55-61.

BELDEN, A. W., DELAMATER, G. R., GROVES, J. W., and WAY, K. M. Washing and coking tests of coal at Denver, Colo., July 1, 1908, to June 30, 1909. *Bull.* 5, Bureau of Mines, 1910, 62 pp.

BEMENT, A. The sampling of coal and classification of analytical data. *Jour. Am. Chem. Soc.*, vol. 28, pt. 1, 1906, pp. 632-639.

BERGIUS, F. Production of hydrogen from water and coal from cellulose at high temperatures and pressures. *Jour. Soc. Chem. Ind.*, vol. 32, 1913, pp. 462-466.

BJÖRLING, P. R. Briquets and patent fuel; their manufacture and machinery connected therewith. 1903. 254 pp.

BJÖRLING, P. R., and GISSING, F. T. Peat, its uses and manufacture.

BRANNT, W. T. Practical treatise on animal and vegetable fats.

BRISLEE, F. J. An introduction to the study of fuel.

CAMPBELL, M. R. Contributions to economic geology, 1907, U. S. Geol. Survey *Bull.* 341, 1909, 444 pp.

—— Contributions to economic geology, 1908, U. S. Geol. Survey *Bull.* 381, 1910, 599 pp.

—— Contributions to economic geology, 1909, U. S. Geol. Survey *Bull.* 431, 1911, 254 pp.

—— Contributions to economic geology, 1910, U. S. Geol. Survey *Bull.* 471, 1912, 570 pp.

—— Contributions to economic geology, 1911, U. S. Geol. Survey *Bull.* 531, 1913, 361 pp.

—— Hypothesis to account for the transformation of vegetable matter into the different grades of coal. *Econ. Geol.*, vol. 1, 1905, pp. 26-33; comment by Lane, A. C., p. 498.

- CAMPBELL, M. R. Classification of coals. U. S. Geol. Survey Prof. Paper 48, pt. 1, 1906, pp. 168-173.
- A practical classification for low-grade coals. Econ. Geol., vol. 3, 1908, p. 134.
- DAVIS, C. A. Uses of peat for fuel and other purposes. Bull. 16, Bureau of Mines, 1911, 214 pp.
- FULTON, JOHN. Coke. 1905. 476 pp.
- FRAZER, PERSIFOR. Classification of coals. Trans. Am. Inst. Min. Eng., vol. 6, 1877-78, pp. 430-451.
- GALE, H. S. Coal fields of northwestern Colorado and northeastern Utah. U. S. Geol. Survey Bull. 415, 1910, 265 pp.
- GROUT, F. F. The composition of coals. Econ. Geol., vol. 2, 1907, pp. 225-241.
- The hydrogen of coal. Jour. Am. Chem. Soc., vol. 29, pt. 2, 1907, pp. 1397-1409.
- LANGMUIR, IRVING. Chemical reactions at very low pressures. Jour. Am. Chem. Soc., vol. 35, 1913, pp. 931-945.
- LEE, W. T. Geology of the coal fields of Grand Mesa and the West Elk Mountains, Colo. U. S. Geol. Survey Bull. 510, 1912, 237 pp.
- LEWES, V. B. The carbonization of coal; a scientific review of the formation, composition, and destructive distillation of coal for gas, coke, and by-products. 1912. 315 pp.
- LORD, N. W., AND OTHERS. Analyses of coals in the United States, with descriptions of mine and field samples collected between July 1, 1904, and June 30, 1910. Bull. 22, Bureau of Mines, 1913, 1200 pp. In two parts.
- MAHLER, P. Expériences sur l'oxydation de la houille. Annales des mines, ser. 11, t. 4, 1913, p. 163.
- PARR, S. W. The available hydrogen of coal. Jour. Am. Chem. Soc., vol. 29, pt. 1, 1907, pp. 582-589.
- The classification of coals. Jour. Am. Chem. Soc., vol. 28, 1906, pp. 1425-1432.
- POOLE, HERMAN. The calorific power of fuels. 1900. 269 pp.
- PORTER, H. C., and OVITZ, F. K. The volatile matter of coal. Bull. 1, Bureau of Mines, 56 pp.
- PORTER, H. C., and RALSTON, O. C. Some properties of water in coal. Technical Paper 113, 1915.
- RANDALL, D. T., and KREISINGER, HENRY. North Dakota lignite as a fuel for power-plant boilers. Bull. 2, Bureau of Mines, 1910, 42 pp.
- SEXTON, A. H. Fuels and refractory materials.
- TAFFANEL, J., LE FLOCH, G., and DURR, A. Oxydation et distillation des poussières.
- WHITE, A. H., and BARKER, PERRY. Coals available for the manufacture of illuminating gas. Bull. 6, Bureau of Mines, 1911, 77 pp.
- WHITE, DAVID. Some problems of the formation of coal. Econ. Geol., vol. 3, 1908, pp. 292-318.
- The effect of oxygen in coal. Bull. 29, Bureau of Mines, 74 pp. Reprint of U. S. Geol. Survey Bull. 382.
- Resins in Paleozoic plants and in coals of high rank. U. S. Geol. Survey Prof. Paper 85 E, 1914, 32 pp.
- WHITE, DAVID, and THIESSEN, REINHARDT. The origin of coal; with a chapter on the formation of peat, by C. A. Davis. Bull. 38, Bureau of Mines, 1913, 390 pp.

PUBLICATIONS ON FUEL TECHNOLOGY.

A limited supply of the following publications of the Bureau of Mines is temporarily available for free distribution. Requests for all publications can not be granted, and applicants should limit their selection to publications that may be of especial interest to them. Requests for publications should be addressed to the Director, Bureau of Mines, Washington, D. C.:

BULLETIN 1. The volatile matter of coal, by H. C. Porter and F. K. Ovitiz. 1910. 56 pp., 1 pl., 9 figs.

BULLETIN 2. North Dakota lignite as a fuel for power-plant boilers, by D. T. Randall and Henry Kreisinger. 1910. 42 pp., 1 pl., 7 figs.

BULLETIN 3. The coke industry of the United States as related to the foundry, by Richard Moldenke. 1910. 32 pp.

BULLETIN 4. Features of producer-gas power-plant development in Europe, by R. H. Fernald. 1910. 27 pp., 4 pls., 7 figs.

BULLETIN 5. Washing and coking tests of coal at Denver, Colo., July 1, 1908, to June 30, 1909, by A. W. Belden, G. R. Delamater, J. J. Groves, and K. M. Way. 1910. 62 pp., 1 fig.

BULLETIN 6. Coals available for the manufacture of illuminating gas, by A. H. White and Perry Barker, compiled and revised by H. M. Wilson. 1911. 77 pp., 4 pls., 12 figs.

BULLETIN 13. Résumé of producer-gas investigations, October 1, 1904, to June 30, 1910, by R. H. Fernald and C. D. Smith. 1911. 393 pp., 12 pls., 250 figs.

BULLETIN 14. Briquetting tests of lignite at Pittsburgh, Pa., 1908-9; with a chapter on sulphite-pitch binder, by C. L. Wright. 1911. 64 pp., 11 pls., 4 figs.

BULLETIN 16. The uses of peat for fuel and other purposes, by C. A. Davis. 1911. 214 pp., 1 pl., 1 fig.

BULLETIN 24. Binders for coal briquets, by J. E. Mills. 56 pp., 1 fig. Reprint of United States Geological Survey Bulletin 343.

BULLETIN 27. Tests of coal and briquets as fuel for house-heating boilers, by D. T. Randall. 44 pp., 3 pls., 2 figs. Reprint of United States Geological Survey Bulletin 366.

BULLETIN 28. Experimental work conducted in the chemical laboratory of the United States fuel-testing plant at St. Louis, Mo., January 1, 1905, to July 31, 1906, by N. W. Lord. 51 pp. Reprint of United States Geological Survey Bulletin 323.

BULLETIN 31. Incidental problems in gas-producer tests, by R. H. Fernald, C. D. Smith, J. K. Clement, and H. A. Grine. 29 pp., 8 figs. Reprint of United States Geological Survey Bulletin 393.

BULLETIN 32. Commercial deductions from comparisons of gasoline and alcohol tests of internal-combustion engines, by R. M. Strong. 38 pp. Reprint of United States Geological Survey Bulletin 392.

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